



CROSS-REFERENCED APPLICATIONS

BACKGROUND OF THE INVENTION

An example of a polymer object used in the dental arts is a composite resin. Most commercial composite resins consist of a resin matrix, an inorganic filler phase and some coupling agents. The resin matrix generally comprises a monomer system, an initiator system and other stabilizers. The monomer system consists of unsaturated compounds. The unsaturated compounds generally comprise one or more esters of ethylenically unsaturated carboxylic acids and the adduct of bisphenol A and glycidyl methacrylate, such

as triethyleneglycol dimethacrylate (TEGDMA), ethyleneglycol dimethacrylate (EGDMA) and 2,2-bis-[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]-propane ether (Bis-GMA) in U.S Patent 3,066,112 to Bowen. Urethane dimethacrylates, such as the 1,6-bis(methacryloyloxy-2-ethoxycarbonylamino-2,4,4-trimethylhexane (UEDMA) which is
5 synthesized from 2-hydroxyethyl methacrylate and 2,4,4-trimethylhexamethylene diisocyanate, are another class of unsaturated material.

The fillers include glasses, ceramics and inorganic oxides, which are generally the oxides of silicon, aluminum zirconium and other transition metals. Some surface treatments, such as silanization, or treatment with titanate, are normally employed before
10 the fillers are used in a composite resin. The fillers commonly have a particle size ranging from 0.04 to 100 microns, and constitute 50 to 80 weight per cent of the composite.

Polymerization of these composite resins is usually achieved by using either chemical or photo-initiated free-radical polymerization. These two methods yield relatively incomplete conversion of the unsaturated compounds. The degree of conversion is
15 generally in the 55-65% range. Incomplete conversion reduces the both mechanical and physical properties of the composite resins, and thus, clinical performance. In addition, unpolymerized monomer can be leached into saliva, and can become a biohazard. Thus, increasing the degree of conversion beneficially would improve the physical and mechanical properties of the composite, while also improving the biocompatibility of the
20 composite resin by reducing the leaching of uncured monomer.

The physical, mechanical and chemical properties of a composite include strength, stiffness, hardness, abrasion resistance, toughness, coefficient of thermal expansion, biocompatibility, and micro-shrinkage. Most properties are derived from all three basic components of the composite, although some are associated with one of the three

constituents. Micro-shrinkage, one of the main shortcomings of composites, is primarily due to the resin matrix. The physical and mechanical properties, such as strength, hardness, stiffness and abrasion resistance, are highly influenced by the resin matrix when the fillers and coupling agents are fixed.

5 Another disadvantage of dental polymers is that they shrink on hardening. This shrinkage compromises the fit, and, in the case of the composite resin, allows for leakage to occur between the composite and the tooth substrate. Although tooth adhesives can compensate somewhat for this shrinkage, bacterial and fluid leakage occurs between the composite and tooth interface, and can lead to diseases of the pulp, which is the vital organ
10 contained within the central part of a tooth, and recurrent caries. Methods that improve the degree of conversion and reduce shrinkage would be very advantageous.

 Improvements in the properties of polymer-containing materials can be obtained by using different processing methods. Composite cure can be enhanced by intensive visible-light exposure, as is done in the Triad device, (Dentsply, USA) or by pressure and
15 heat curing (Ivoclar, Schaan, Liechtenstein). These improvements still result in incomplete and less than satisfactory polymerization, as well as varying degrees of micro-shrinkage. Furthermore, improvements which substantially increase the degree of conversion generally require a laboratory step. Thus, in the dental arts, a highly precise replication of the body tissue is made, a replica is made, and an object is prepared using that replica. This requires
20 two visits. The two visits and the laboratory procedure can be costly and constitute further disadvantages.

 Microwave energy has a utility in the processing of polymers. Interest in microwave/radio frequency heating has increased over the last 30 years because of the continuous development of equipment capable of operating in an industrial environment.

Conventional heating is concerned primarily with a relatively high-temperature heat source interacting with a relatively low-temperature product surface. In the absence of evaporation or other change of state, the rate of heating and temperature distribution from the surface inwards is governed by the thermal conductivities and specific heats of various constituents of a material. Usually, the rate of heating is slow, so that heat transfer by thermal conduction minimizes the temperature differences that would otherwise exist because of different specific heats; therefore, a relatively uniform temperature gradient from the warm surface to the cooler center of the material is found. In conventional heating, the usual thermal properties such as specific heat, thermal conductivity, coefficient of expansion and emissivity do not change significantly over the usual temperature range of the process.

The main advantages provided by microwave energy include: (1) good penetration, fast heating rates and shorter curing time, which results in a reduction in the distortion; (2) minimal thermal lag and thermal gradients, which results in a more homogeneous cure and better mechanical properties.

Microwave curing of composites under pressure is one way of reducing polymerization shrinkage. Microwave curing of composites while injected into a mold further reduces porosity, and enhances density, and consequently improves the survival of the dental restoration.

The residual monomers (unbound materials) in the composite can be leached which is yet another problem. The leaching has an adverse impact on both structural stability and biocompatibility. The residual monomers are eluted into salivary fluids and brought into contact with mucosal tissues; or be extracted into dentin and diffused into the pulp. The elution decreases with the higher degree of conversion. An increased degree of conversion will result in improved mechanical properties and biocompatibility of composite.

Denture liners are further examples of a polymer object. Several kinds of soft denture liners are used, and include polysiloxane, polyurethanes, plasticized polymethacrylates, polyvinyl chlorides and polyphosphazene fluoroelastomers.

Most soft-liners have inherent disadvantages. These include the leaching of potentially harmful bonding agents, such as epoxy and urethane adhesives, sulfuric, perfluoroacetic acid; poor adhesion to the polymethylmethacrylate (PMMA) denture base due to the chemical dissimilarities between liners such as hydroxyl-terminated polydimethylsiloxane and PMMA; porosity in denture base and the liner resulting from vaporization of the solvent; dimensional changes caused by micro-shrinkage, or dehydration and rehydration steps.

The improvements of denture liners may be based on the use of novel materials, such as acryloxy or methacryloxy polydimethylsiloxanes and acryoxyalkyl or methacryloxyalkyl-terminated polydialkylsiloxanes which have been recently introduced. Since these organosilicons have similarities with PMMA, the bonding between liners and the denture is improved, and use of bonding agents is avoided. However, the curing time for these liners, is relatively long.

Once hardened, on seating of the denture, the oral tissues are subjected to change and compression. A way to improve the fit of existing dentures is to, retake an impression, and have a denture rebased. This procedure is usually done in a laboratory, and the material characteristics are deficient in a manner similar to the materials that undergo water-bath hardening. In addition, the procedure takes two visits, is more time consuming, which are factors adding to the cost of the procedure. Chairside relines can be made using chemically-cured polymers, such as methylmethacrylates, polymethylmethacrylates, polyvinyl acrylates, 2, 2-bis [(p-2'hydroxy-3'methacryloxy-propoxy) phenyl] propane,

triethyleneglycol dimethacrylate, urethane dimethacrylate, or light-cured polymers.

However, they have a relatively low degree of cure, are extremely porous since no compression is possible, and often can cause chemical and physical irritation of the oral tissues.

5 Problems existing in dental objects made of, or containing polymers may be caused by relatively incomplete degree of conversion, micro-shrinkage, and porosity. An increase in the degree of conversion, a decrease of micro-shrinkage, and a decrease in porosity will result in improved performance of these objects. Furthermore, a processing which more rapidly imparts improvements will have a greater utility for the dental profession. This can
10 be achieved by microwave heating.

Microwave heating is uniquely different because heat is generated within the material rather than being generated externally. The dielectric properties that govern the rate of internal heating may vary widely in magnitude among various constituents of a multiphase, multi-component product. Furthermore, they may change very significantly
15 with temperature. Therefore, the temperature distribution at a given time in a microwave/RF heated material will depend primarily on the dielectric properties, specific heats and thermal conductivity's of the material's constituents. The thermal conductivity's of the constituents may tend to equalize the local temperature variations, but often, the rate of heating with microwave energy is so high that internal conduction of heat cannot transfer
20 the accumulated heat throughout the material.

The permittivity characteristics of polymers with or without filler at various frequencies and at various temperatures are published in the literature. Von Hippel presents a table of data at frequencies from 100 to 1010 Hz for various polymers and compounds. Ippen presents, in graphical form, the loss factors of various polymers, blends of polymers

and polymers with various fillers as a function of temperature at 3 Ghz. The selection of the proper frequency in microwave/RF heating is based on important parameter of the product of relative loss factor, ϵ'' , by frequency, f . The power absorption capacity of a material depends mainly on, ϵ'' , f and its geometrical shape. Since the shape is variable, the only way to evaluate the heatability of materials is to examine the product, $\epsilon'' f$.

SUMMARY OF THE INVENTION

An object of this invention to identify polymerizable microwave-sensitive compositions having primary use in the biomedical field, and in particular, in the dental arts, although the materials can be used elsewhere whenever rapid processing of precise shapes are required.

It is an object of this invention to introduce the compositions into a chamber, whereby hydraulic pressure is used to inject the material into a three-dimensional mold, the mold constituting a replica of a body part, and having an air escape vent.

It is an object of this invention to maintain pressure on the said compositions while the composition is in the mold.

It is an object of the present invention to harden the compositions using microwave energy, delivered to the mold which is contained in a microwave chamber.

It is an object of this invention to perform an *in situ* (directly in the mouth) hardening of the said polymerizable composition used for the restoration of teeth using a hand-held apparatus placed in the vicinity of the composition, which has been placed in a tooth.

BRIEF DESCRIPTION OF THE FIGURES

Figures 1a and 1b relate, respectively, to spectra of uncured and cured PMMA.

DETAILED DESCRIPTION OF THE INVENTION

5 In dental arts, various compositions are useful for the construction of dental devices comprised in part, or in whole, of polymers. These compositions may be used in the filling of teeth and the construction of appliances used for replacing teeth and other oral structures. One utility of these compositions is in the restoration of lost tooth tissue, while another is in the construction of removable dental appliances including (such as dentures, soft and hard
10 relines). The compositions in this invention are also useful for the construction and forming of composite fillings crowns, bridges, inlays, onlays, temporary prostheses, inlays or onlays, facings, veneers, orthodontic appliances.

A preferred composition for a dental composite adapted to cure with the method and apparatus of this invention include:

15 (I) polymerizable resin suitable for use in the oral environment, which comprise 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (BisGMA) (ratio), ethyleneglycol dimethacrylate (EGDMA) and triethyleneglycol dimethacrylate (TEGDMA), eutectic monomers, hydrophobic (hydrophilic) monomers, urethane dimethacrylate resins, spiro orthocarbonates, organo-esters of phosphorus; (II) inorganic or
20 organic fillers; and (III) coupling agents and other additives.

A preferred embodiment of the composition for a dental composite in accordance with this invention consists of (I) a polymerizable resin suitable for use in the oral environment, which includes 2,2-bis[4-(2-hydroxy-3-

methacryloyloxypropoxy)phenyl]propane (BisGMA), ethyleneglycol dimethacrylate (EGDMA) and triethyleneglycol dimethacrylate (TEGDMA), urethane dimethacrylate, eutectic monomers, hydrophobic monomers, urethane dimethacrylate resins, spiro orthocarbonates, organo-esters of phosphorus; (II) inorganic or organic fillers as described; (III) polyfunctional coupling agents, such as gamma-methoxypropylene silane, or a silane-containing coupler which can form siloxane linkages with inorganic particles and co-polymerizes with a polymer matrix, or an alkylthiol having a methacrylate functionality, such that the thiol end forms a self assembled monolayer on the metal particles, and the methacrylate functionality co-polymerizes with a polymer matrix, and other additives. The weight % of the organic filler as an overall weight of the composite can be in the range of 30 to 96%, but preferably in the range of 50 to 75%.

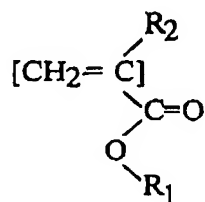
The composite contains organic peroxide microwave sensitive polymerization initiators. The organic peroxide in accordance with this invention comprises benzoyl peroxide, dilauroyl peroxide, (tert-butyl peroctoate or tert-butyl perbenzoate, 2,4-dichlorobenzoyl peroxide and 4,4-dichlorobenzoyl peroxide) in the weight range of the composition of 0.05% to 1.0 %, preferably in the range of 0.09 to 0.5%, and amine accelerators, comprising N, N-diethenol-p-toluidine, or triethylamine.

The polymerizable resin combinations include Bis-GMA and TEGDMA, and can have a mixture ratio of 0.3 to 0.7, preferably in the range of 0.5, and are suitable in practicing the disclosed method and for use in combination with an apparatus disclosed, when used together with microwave sensitive polymerization initiators for making and using the curable material system. Urethane dimethacrylate can be substituted for TEGDMA.

aluminosilicate with a zeolite structure), and fluorides of the rare earth metals or mixtures of such fluorides (glass pyrogenically produced), ceramics, zirconium. They comprise particle sizes ranging from 0.04 micrometers to approximately 10 micrometers, preferably being distributed between 1 and 7 micrometers. Composites can also exclusively contain submicron colloidal silica, or pre-polymerized polymer containing colloidal silica. They can also contain metal particles having sizes ranging from 0.04 micrometers to approximately 10 micrometers, preferably being distributed between 1 and 7 micrometers. The metal particles can be pure gold, or silver, or alloys of silver and tin, which may be surface-modified with a coating of pure silver or pure gold.

Compositions that are especially suitable for removable dental prostheses comprise a liquid component (i) and a powdery component (ii). The liquid component (i) contains from 20% to 98%, more preferably from 30% to 95%, and most preferably from 40% to 90% of mono-, di-, tri-, or multifunctional acrylic monomer. Advantageously, the liquid component in accordance with the invention includes a plasticizer, an accelerator and a cross-linking agent.

The mono-, di, tri, or multifunctional acrylic monomer in accordance with the invention are within the scope of the general formula (I) :



wherein R_1 represents hydrogen, an alkyl group, a substituted alkyl group, a cyclic hydrocarbon, benzyl, ether, hydroxyalkyl and R_2 represents hydrogen, halogen, an alkyl group, a substituted alkyl group or a cyclic hydrocarbon group. These monomers may be used alone or in admixture.

5 A microwave sensitive initiator system comprises, a peroxide such as benzoyl peroxide, dilauroyl peroxide, tert-butyl peroctoate, tert-butyl perbenzoate, 2,4-dichlorobenzoyl peroxide or 4,4-dechlorobenzoyl peroxide. The cure accelerator in accordance with the invention is a quaternary ammonium chloride, which is easily soluble in the methacrylate monomers and reacts with barbituric acid derivatives. The preferred
10 quaternary ammonium chloride compounds are quaternary ammonium chloride having with an alkyl of 1 to 20 carbons, such as, dodecyltrimethylammonium chloride, lauryldimethylammonium chloride, dimethyldioctadecylammonium bromide dioctyldimethylammonium chloride. Quaternary ammonium chlorides may be added alone or in admixture.

15 The crosslinking agent included in the microwave curable material composition is a polyfunctional monomer wherein at least two carbon-carbon double bonds, such as 1,3-butanediol dimethacrylate, 1,4-butanediol dimethacrylate, 1,4-butanediol divinyl ether, di(ethylene glycol) dimethacrylate, di(ethylene glycol) divinyl ether, pentaerythritol diacrylate monostearate, ethylene glycol dimethacrylate, trimethylolpropane
20 trimethacrylate, pentaerythritol triacrylate, pentaerythritol triallyl ether, pentaerythritol tetra-acrylate, trimethylolpropane triacrylate. Crosslinking agents may be used alone or in admixture.

A cure promoter for the monomers in curable material system (such as acrylates) is needed. When these compositions are irradiated with microwaves, barbituric acid

derivatives rapidly react with the quaternary ammonium chloride to produce radicals, which promote a rapid and uniform polymerization in the composition and a higher degree of conversion. The barbituric acid derivatives in accordance with the invention include 1,3,5-trimethylbarbituric acid, 1,3-dimethyl-5-isobutylbarbituric acid, 1,3-dimethyl-5-phenylbarbituric acid, 5-n-butylbarbituric acid, 5-ethylbarbituric acid, 5-phenylbarbituric acid, 1-cyclohexyl-5-ethylbarbituric acid and 1-benzyl-5-phenylbarbituric acid. These acid derivatives may be used alone or in admixture.

A polymerization inhibitor, such as hydroquinone, 4-ethoxyphenol, 2-hydroxy-4-methoxybenzophenone, may be added to the liquid to keep the storage stability up to three years.

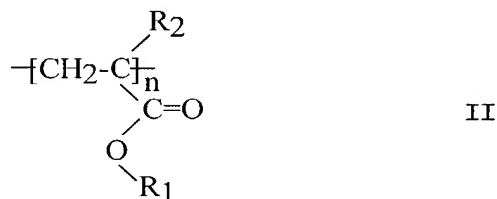
The plasticizer in accordance with the invention is generally a low molecular weight ester, such as dibutyl phthalate or phosphates .

The composition for a one component microwavable curable denture base in accordance with this invention is approximately the same as the one for the two component materials with some variations mainly in the initiation system. Preferred initiators used in one component denture base are be thermally stable at room or higher temperatures such as 60°C and initiate polymerization at higher temperatures. Suitable initiators include benzopinacole, tert-butyl perbenzoate, and tert-butylperisononanoate (ratio, temperature).

The powder component in accordance with the invention includes from 15% to 90%, more preferably from 30% to 75%, and most preferably from 45 to 70% by weight of mono-di-tri, or multifunctional acrylic or acrylate ester polymer. The powder may advantageously include from 0% to 70%, preferably from 1.5% to 60%, and most preferably from 3% to 40% of a copolymer. The powder component in accordance with the invention may advantageously include 0% to 15%, more preferably 0.1% to 10%, and most

preferably from 3% to 40% of a copolymer. The powder component in accordance with the invention may advantageously include 0% to 15%, more preferably 0.1% to 10%, and most preferably 0.1% to 5% and especially preferably 0.1 % to 3 % of an initiator (for radical polymerization) such as organic peroxide. The powder component in accordance with the invention can include up to 5%, preferably up to 3%, more preferably up to 1% of a barbituric acid derivative, to promote chemical reaction.

The mono-, di, tri, or multifunctional acrylic polymer(s) used in a denture base according to the present invention have a molecular weight of at least 143 and are represented by the general structural formula (II):



wherein R₁ represents hydrogen, an alkyl group, a substituted alkyl group, a cyclic hydrocarbon, benzyl, ether, hydroxyalkyl; R₂ represents hydrogen, halogen, an alkyl group, a substituted alkyl group; and n is an integer at least equal to 2.

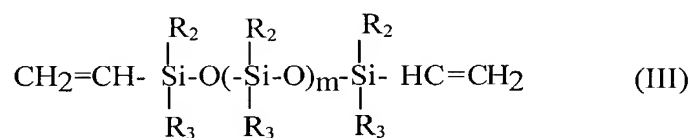
In accordance with this invention, the polymer is composed mainly of methyl methacrylate polymer or a mixture of methyl methacrylate polymer and a methacrylate polymer other than methyl methacrylate polymer with the general formula (II), wherein R_1 is neither hydrogen or methyl. Inorganic and organic fillers may be added into the compositions of one or two components denture base.

Useful inorganic fillers include glass, metal ceramics, silicon in powdery or fiber format, which are preferably silaned with coupling agent such as 3-methacryloxypropyltrimethoxy silane by the common techniques used in dental science. Organic fillers include splinter or bead polymers of high molecular weight, or fibers such as carbon fibers, aramide fibers, polyethylene fibers, polyacrylate fibers, polyester fibers, polyamide fibers and polyacrylonitrile fibers. Organic fillers may be used alone or mixed with inorganic fillers.

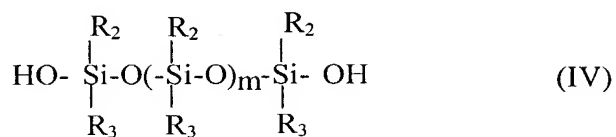
Soft material composition for applications such as denture liners formed and cured with the present novel method include one and two component compositions: (I) an amount of one or more organopolysiloxanes, preferably methacryloxypropyl-terminated polydimethyl siloxanes, a crosslinking agent which contains at least two functional groups and an initiator and (II) an amount of a phosphonitrilic fluoroelastomer, such as poly(fluoroalkoxy)phosphazene, [a crosslinking agent which contains at least two functional groups, a filler and an initiator].

Orgnaopolysiloxanes and phosphonitrilic fluoroelastomers are particularly suitable as microwave-curable soft material systems useful in the method according to the present invention. (With the exception the high degree of thermal and oxidative stability, low degree of toxicity and high chemical inertness, organosilicon is very resilient as a result of the motions of Si-O-Si and Si-C bonds in the main and side chains). The

organopolysiloxanes in the compositions for soft denture liners in accordance with the invention are within the scope of the general structural formula (III):



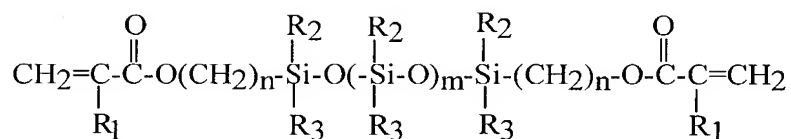
(IV)



wherein m is an integer having a value from 1 to about 6,000; n is an integer having a value from 1 to 6; R₁ represents hydrogen or alkyl group, R₂ and R₃ represent alkyl groups having 1 to 6 carbon atoms. The most preferred polysiloxanes is the methacryloxy-terminated polydimethylsiloxanes represented by the formula (V). The adhesion of methacryloxy-

terminated polydimethylsiloxanes to PMMA is improved due to the chemical similarity between these two materials.

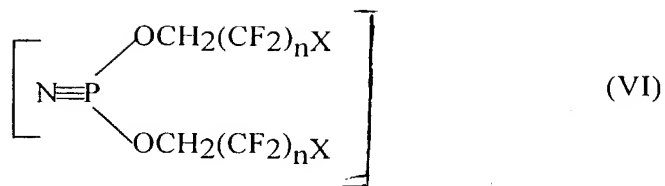
(V)



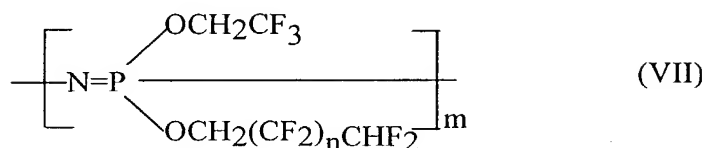
5 The crosslinking agent in accordance with the invention may be used in the soft denture liners. The crosslinking agents are normally multifunctional monomers having at least two carbon-carbon double bonds. The most preferred crosslinking monomers are acryloxy or methacryloxyalkyl-terminated siloxane monomers, such as 1,3-bis[(p-
acryloxymethyl) phenethyl] tetramethyldisiloxane, 1,3-bis(3-methacryloxypropyl)
10 tetramethyldisiloxane (MPTDS), due to the similarity between crosslinking agent and organopolysiloxanes.

In general, initiators for use in the soft denture liners in accordance with the invention are peroxides, such as benzoyl peroxide, lauroyl peroxide, tert-butyl peroctoate or tert-butyl perbenzoate.

15 Phosphonitrilic fluoroelastomers in accordance with this invention are polymerized by monomer represented by the general formula (VI):



wherein X represents H or F, and n is usually from 1 to 11. This material is commercially available as EYPEL-F from Phosphazine Custom Synthesis:



5 wherein n is 3, 5, 7, 9, or 11, and m is from 10,000 to 50,000. In order to minimize the absorption of water, the NaCl contained in the EYPEL-F should be removed by extraction and coagulation from acetone.

The crosslinking agents suitable for the fluoroelastomers are the monomers with at least two functional groups, such as tetraethylene glycol dimethacrylate (TEGDMA),
 10 ethylene glycol dimethacrylate (EGDMA), 1,6-hexamethylene glycol dimethacrylate (HGDMA), trimethylpropane trimethacrylate (TMP-TMA), pentaerythritol triacrylate, pentaerythritol triallyl ether, pentaerythritol tetraacrylate.

The fillers improve hardness and the ability to grind and polish the cured fluoroelastomer and improve the bond strength between the liner and base due to the

At this time, the material is hardened by the microwave energy, while the mold is rotating. The time of exposure will vary from 1 to 50 minutes, this being dependent on the size and particular composition of the object.

In a preferred embodiment for the fabrication of composite resin inlays and crown for the restoration of teeth, a hand-held reduced size microwave emitting device is brought to the tooth to expose a composite resin formulation that has been placed in the tooth. The frequencies emitted can be 2.45 GHz, or preferably, or at 15, 18, 22, and 28 GHz. The optimal frequency will be determined by the permittivity of the polymerizable composition being used.

It should be understood that the present invention has been described in considerable detail with respect to certain specific embodiments thereof. However, the present invention should not be considered limited to such embodiments but may be used in other ways without departure from the intent of the invention and the scope of the claims.

Example 1.

The effect of microwave curing on dental polymers was measured. Bars conforming to the ISO standard for measuring flexural strength were made using a resin mixture consisting of BIS-GMA:TEGDMA at a 1:1 ratio. Bars were either cured chemically (n=4), by visible light (n=5), or microwave energy (n=4). Cured samples were subjected to a three-point bend test, and flexural strength calculated. The mean values in MPa and (standard deviations) for each of the samples respectively were 18.5 (4.4), 45.9 (7.3), and 59.0 (6.9). Analysis of the means by a one-way ANOVA gave a p value <0.001. Post-hoc comparisons using Tukey's method indicated that differences between all groups were significant (p<0.05), and that the microwave cure significantly increased.

Example 2.

To evaluate the effect of microwave curing on the degree of conversion of a microwave sensitive composition consisting of polymethylmethacrylate (PMMA), spectra of uncured and cured PMMA (Fig. 1(a) and 1(b)) were recorded using FT-Raman spectroscopy. The C=C peak (the unsaturated carbons) is observed at 1602 cm^{-1} in the uncured sample in 1(a). The peak virtually disappears in the cured sample 1(b), indicating that the degree of conversion is nearly complete. The degree of conversion is calculated by the method described by Ferracane, and was determined to be 92%.